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by

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Supercell Calculations of Positron Trapping and Annihilation at Vacancies in Simple and Transition Metals*

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A new approach, based upon augmented-plane-wave calculations in a supercell lattice, has been developed to theoretically predict the annihilation characteristics of the positron in vacancies, taking into account for the first time the atomic nature of the solid. This method, which is general and suited equally well to both simple and transition metals, has been used to calculate positron trapping and annihilation characteristics in Al, Nb, Ta, and W. The results indicate that the positron is sufficiently strongly trapped in a vacancy in all of these metals that significant thermal detrapping in any of them is highly unlikely.

Positron annihilation spectroscopy (PAS) has established itself as a rather powerful tool in the study of vacancies and vacancy-like defects in metals. Despite much experimental PAS work during the last decade, the theoretical effort in this area has been rather limited. Needless to say, a microscopic understanding of the characteristics of positron annihilation depends on an understanding of the underlying mechanism of electron-positron overlap that determines these characteristics. Within the independent particle model (IPM) the latter have heretofore been discussed, for the positron in a vacancy, on the basis of the jellium description of a metal, which omits the effects of the ion-core lattice. The jellium approximation has two important consequences. First, it does not allow for the calculation of the core-electron contribution to either the positron lifetime or the 2γ angular correlation curves. As such, this contribution has either been neglected or taken into account on an ad hoc basis. Second, since only the electron density resulting from these calculations has any meaning and the eigenfunctions are not the true eigenstates of the system, the electron-positron momentum distribution, which depends explicitly on the Fourier transform of the overlap of both the electron and positron wavefunctions, must be expressed in terms of the overlap of the electron and positron densities. Additional approximations have therefore been necessary in the calculation of the angular correlation curves. It is thus clear that this simplified model does not do justice to the true situation, since in the final analysis it amounts to ignoring the nondiagonal terms of the electron-positron overlap density matrix so that the net result can be expressed only in terms of the diagonal elements. These nondiagonal elements are, however, quite important for the angular correlation curves, since for nonzero momenta the nondiagonal terms are the only contributors to the momentum distribution. In addition to the jellium model being too simplistic, it is also restricted in its scope to 'simple metals'. The class of transition metals, which are of particular interest both scientifically and for their technological applications, are beyond the scope of these models.

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The purpose of this paper is to present a general approach developed by the present authors [1] to theoretically predict the annihilation characteristics of the positron in vacancies. This approach, which is applicable to both transition and simple metals, is based upon the augmented-plane-wave (APW) method of band theory and employs a supercell lattice to represent the environment of a vacancy (see inset to Fig. 1). Since the atomistic nature of the solid is fully included in this approach, none of the approximations of the jellium type appear in the calculations of the annihilation characteristics. In particular, the angular correlation curves can be calculated exactly within the IPM and the core-electron contribution to both the lifetime and the angular correlation curves can be properly included. The results for Al and the first theoretical results for the bcc refractory metals Nb, Ta, and W are discussed in this paper.

For both fcc (Al) and bcc (Nb, Ta, W) metals a supercell with a volume 27 times that of the corresponding primitive unit cell was chosen. The origin of coordinates was placed at the vacancy which was located at the center of the supercell. The presence of the vacancy causes the various atomic shells surrounding it to experience different environments and hence different potentials. These shells have thus been treated differently. This is essentially equivalent to a band-structure problem with four different atomic species in the supercell. The crystal potentials for the electrons and positron were obtained by superposition of the self-consistent Hartree-Fock-Slater atomic charge densities [2] and atomic potentials that were obtained from the solution of Poisson's equation. The exchange and correlation contribution to the electronic potential was included using the Xα method with the Slater exchange parameter $\alpha = 1.0$. For the positron potential the Slater term was not included, since there is no exchange contribution in that case. The crystal potential was made spherically symmetric inside each muffin-tin sphere, but was not assumed constant in the interstitial region between the muffin-tin spheres and warping corrections were included.

Two states of the positron at the zone center were found, a bound state in the vacancy and a higher energy state, usually referred to as the Bloch state, which lies at the bottom of the positron conduction band. The depth of the trapping potential at the center of the vacancy, V_t, and the binding energy of the positron to the vacancy, E_b, both measured from the Bloch state of the positron, are given in Table 1 for the four metals studied Al, Nb, Ta,

Table 1. Pertinent parameters and results for Al, Nb, Ta, and W.

	Al	Nb	Ta	W
a (Å)	4.0496	3.3004	3.3058	3.1647
T_m (K)	933	2741	3270	3695
V_t (eV)	10.46	13.60	13.89	14.73
E_b (eV)	3.36	4.62	4.94	5.45
Q_1 (eV)	1.28[a]	3.62[b]	4.07[a]	5.45[c]

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and W. The calculations refer to the respective lattice parameters (a) at room temperature. The trapping potentials are not constant inside the muffin-tin spheres, and show a variation of ∿3 eV from the center of the vacancy to the surface of its muffin-tin sphere. Table 1 shows that the trapping potentials in all four metals are rather large ($\gtrsim$ 10 eV), and result in large positron-vacancy binding energies and strong localization of the positron in the vacancy. In the Bloch state the positron is pushed into the interstitial region due to repulsion from the ion-cores, while in the vacancy-trapped state a strong localization of the positron results [3,4]. This can be seen in Fig. 1 where we have shown the positron density in its vacancy-trapped state in Al. An analysis of the positron charge density shows that the vacancy muffin-tin sphere, with a volume of only 2.5% of the volume of the supercell, contains more than 50% of the positron charge in the case of Al and ∿55-60% in the cases of Nb, Ta, and W. The positron density inside the vacancy muffin-tin sphere shows relatively little anisotropy. However, the anisotropy is rather substantial in the interstitial region surrounding the vacancy. This results from the atomic nature of the solid and has important consequences for the calculated positron lifetime and angular correlation curves, since the electron-positron overlap is largest in the interstitial region.

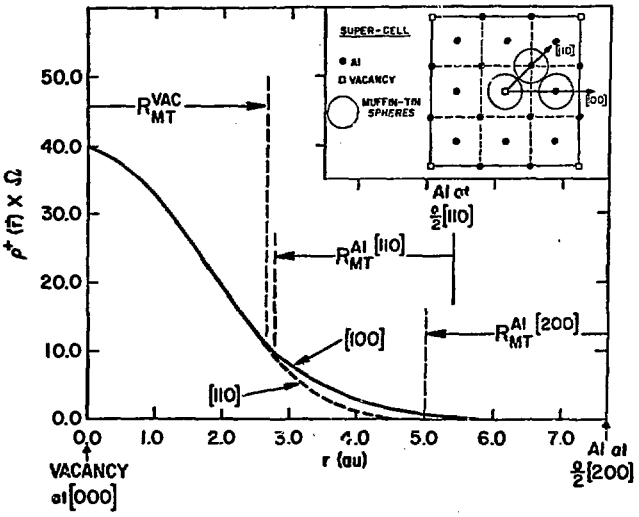

Fig. 1. The positron density $\rho^+(\vec{r})$ in the vacancy-trapped state in Al along the [100] and [110] directions multiplied by Ω, the volume of the supercell [1]. R_{MT} denotes the radius of the muffin-tin sphere. The (001) face of the face-centered cubic supercell for Al is shown in the inset.

As seen in Table 1, the calculated positron-vacancy binding energies increase systematically for the three refractory metals Nb, Ta, and W. For these high melting temperature (T_m) metals with, presumably, rather high vacancy formation enthalpies, some concern has been expressed [5,6] that thermal detrapping of positrons could affect the determination of vacancy formation enthalpies by PAS. The values of E_b are, however, all larger than or equal to the respective activation enthalpies (Q_1) for self-diffusion via a monovacancy mechanism in these metals. Since $Q_1 = H_{1v}^F + H_{1v}^M$, where H_{1v}^F and H_{1v}^M are the monovacancy formation and migration enthalpies, respectively, it can be seen that $E_b > H_{1v}^F$ in all three metals. The ratio of positron detrapping to trapping at equilibrium is proportional to $\exp[-(E_b - H_{1v}^F)/kT]$. Thus, it can be concluded that positron detrapping in Nb, Ta, and W is highly unlikely, since even for the case of W, the only one of these metals for

which the value of H_{1v}^F ($\approx 3.7 \pm 0.2$ eV) is already reasonably well established [7,8], the value of E_b is almost 2 eV greater than H_{1v}^F. Although atomic relaxation around the vacancy has not been included in the present calculations and one may expect its inclusion to affect the calculated magnitudes of V_t and E_b, the systematics of the results for Nb, Ta, and W, and hence the conclusions, are unlikely to be changed. Furthermore, the localization of the positron in a vacancy will tend to cancel the effects of atomic relaxation [9]. These conclusions thus contradict the interpretation by Maier et al. [5,6] of their data, in which thermal detrapping in Ta was suggested. Their choice of an anomalously smaller value of their W-parameter for the positron in its vacancy-trapped state relative to that in its Bloch state for Ta, as opposed to W, presumably forced their invocation of thermal detrapping in Ta in order to obtain reasonable values of the vacancy formation enthalpy and the vacancy concentration.

Calculations of the core contribution to the angular correlation curves, both in the Bloch and the vacancy-trapped states of the positron in W, have also been completed [4], but cannot be discussed here for lack of space. For Al the calculated angular correlation curves, including both core and valence electron contributions, in the two states of the positron are in good agreement with the available experimental data [3]. In addition, the temperature dependences of the positron lifetime in the two states, associated only with the thermal expansion of the lattice, have been calculated. It has been found that, contrary to the usual belief, the fractional increase of the positron lifetime in Al in the Bloch state is only $\sim$80% of that expected from the volume expansion of the lattice. This reflects simply the redistributon of the positron and the changed electron-positron overlap in an expanded lattice. The lifetime in the vacancy-trapped state was also found to vary with temperature, and shows a fractional increase of $\sim$50% of the fractional increase in the volume of the lattice. These results are consistent with the experimental results of Fluss et al. [10]. For further details, the reader is referred to Ref. [3].

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